

Japanese Patent Laid-Open No. 61-133560

Specification

1. Title of The Invention

Zinc Alkaline Cell

2. Claim

A zinc alkaline cell using a zinc electrode, the surface of which is amalgamated with mercury oxide powder by adding zinc powder to a gelled alkaline electrolyte in which the mercury oxide powder is dispersed.

3. Detailed Description of The Invention

[Field of The Invention]

The present invention relates to the improvement of a zinc alkaline cell using zinc as an active material for a negative electrode, an aqueous alkali hydroxide solution as an electrolyte, and manganese dioxide, silver oxide, mercury oxide, oxygen or the like as an active material for a positive electrode.

[Description of The Prior Art]

There is a problem in that zinc serving as an active material for a negative electrode is corroded in the presence of an alkali electrolyte during preservation. Conventionally, as an industrial technique, there is a technique for using amalgamated zinc powder, which is prepared by adding 5 to 10 wt% mercury to zinc, to increase a hydrogen overvoltage to inhibit corrosion to such an extent that there is no problem for practical use. However, in recent years, it is desired to reduce the content of mercury in cells to reduce environmental pollution, so that various studies have been made. For example, in a conventional zinc powder amalgamating method, i.e., in a method for preparing amalgamated zinc powder by dropping metallic mercury into zinc powder in an aqueous alkali solution to agitate the solution to amalgamate the zinc powder to wash and dry the amalgamated zinc powder, mercury is dropped gradually and in the form of fine particles, or a method for agitating the solution so that zinc particles can contact each other as well as possible is selected, in order to achieve a uniform concentration of mercury in zinc powder. However, if only such an improvement is made, although it is possible to slightly uniformly amalgamate atomized zinc powder, agitation time increases. For that reason, zinc particles are destroyed

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during agitation, so that it is not possible to reduce the amalgamation rate. In addition, there is provided a method for reducing the amalgamation rate using zinc alloy powder, the corrosion resistance of which is improved by adding lead, gallium, thallium, indium, cadmium or the like to zinc. This method has an effect on the inhibition of corrosion to some extent, and the amount of mercury can be slightly reduced. However, other elements, which may cause other environmental pollution, are added, so that it is difficult to put the above method to practical use unless it is determined from various sources if the added elements cause environmental pollution.

[Problem to be Solved by The Invention]

Thus, it is strongly desired to provide a zinc negative electrode for use in a zinc alkaline cell, which has a low amalgamation rate and excellent corrosion resistance.

It is an object of the present invention to provide a low-pollution zinc alkaline cell capable of reducing the amalgamation rate without deteriorating corrosion resistance of a zinc negative electrode.

[Means for Solving The Problem]

The present invention is characterized that a zinc negative electrode of a zinc alkaline cell using an electrolyte of an aqueous alkaline solution containing sodium hydroxide, potassium hydroxide or the like as a major component, zinc as an active material for a negative electrode, and manganese dioxide, silver oxide, mercury oxide, oxygen or the like as an active material for a positive electrode is a gelled zinc negative electrode, the surface of which is amalgamated by adding zinc powder to a gelled alkali electrolyte, in which mercury oxide powder is dispersed.

[Operation]

The present invention utilizes a reaction for producing zinc oxide and metallic mercury by contacting mercury oxide with zinc in an alkaline electrode. The surface of zinc powder is amalgamated with the produced metallic mercury. The mercury oxide powder is fine powder having a mean grain size of about ten microns. Therefore, if the mercury oxide powder is dispersed in a gelled alkaline electrolyte to add and agitate zinc powder having a mean grain size of one hundred and tens microns to react the zinc powder with the mercury oxide powder, the zinc powder is amalgamated while individual zinc particles are sufficiently covered with mercury oxide

particles, so that the zinc particles can be very uniformly amalgamated. In addition, since the zinc particles are suspended and dispersed in the gelled alkaline electrolyte, there is hardly any stress applied to the zinc particles by an agitator, such as a stirrer. Therefore, the zinc particles are not destroyed unlike the conventional method for agitating an aqueous alkali solution, so that it is possible to improve corrosion resistance.

As described above, the present invention realizes a zinc negative electrode having excellent corrosion resistance and a low amalgamation rate by amalgamating the surface of zinc powder, which is used for a negative electrode, with fine mercury oxide powder in a gelled alkali electrolyte.
[Description of Preferred Embodiments]

Mercury oxide powder having a mean grain size of 15 microns is added to a gelled alkaline electrolyte, which is gelled by adding a polyacrylic sodium to a 40 wt% aqueous potassium hydroxide solution to agitate the solution, to be agitated and dispersed. To this solution, zinc powder having a mean grain size of 150 microns is added, and agitation is continued until the surface of the zinc powder is completely amalgamated. The progress of amalgamation can be confirmed on the basis of the degree of dissipation of suspended mercury oxide. Usually, the zinc powder to be added to the gelled alkaline electrolyte is preferably in the range of from 100 to 250 % by weight. In this range, amalgamation can be completed within 1 hour. The mercury oxide may be added to the gelled alkaline electrolyte after adding the zinc powder. However, in this case, amalgamation is slightly ununiform to be uneven.

By the above described method, gelled zinc negative electrodes, which include 150 wt% zinc powder with respect to the gelled alkali electrolyte and which have amalgamation rates of 1, 3, 5 and 7 wt% were prepared, respectively. As comparative examples, amalgamated zinc powders having amalgamation rates of 1, 3, 5 and 7 wt% were prepared by the conventional method for dropping metallic mercury in an aqueous alkali solution to amalgamate zinc powder, and the amalgamated zinc powders were dispersed in a gel electrolyte at the same rates as those in the above described preferred embodiment to prepare gelled zinc negative electrodes.

Table 1 shows hydrogen gas generating rates when the gelled zinc negative electrodes were preserved at 45°C for 40 days.

Table 1 (unit: $\mu\text{l/g} \cdot \text{day}$)

Amalgamation Rate	1%	3%	5%	7%
Amalgamated Electrode based on mercury oxide powder	15.4	6.2	5.1	4.8
Amalgamated Electrode based on metallic mercury	94.5	38.3	6.8	4.9

As can be seen from this table, in the conventional method, the hydrogen gas generating rate, i.e., the corrosion rate of the zinc negative electrode, rapidly increases when the amalgamation rate is less than 3%, whereas in this preferred embodiment, the hydrogen gas generating rate at an amalgamation rate of 3% is less than that at an amalgamation rate of 5% in the conventional method, so that the amalgamated negative electrode in this preferred embodiment has excellent corrosion resistance.

Then, a button-type alkaline manganese cell shown in the drawing was prepared using the gelled zinc negative electrode which was used for the above described hydrogen gas generating tests. Reference number 1 denotes a metal sealing plate, reference number 2 denotes a sealing gasket, and reference number 3 denotes a cylindrical metal case with bottom. On the inner bottom of the case 3, a positive electrode mixture 4, which is previously formed of a tablet of a mixture of manganese dioxide and graphite, and a positive ring 5 are pressingly applied. Reference number 6 denotes a separator of a porous synthetic resin film, reference number 7 denotes a cellulose liquid holding member, and reference number 8 denotes a gelled zinc negative electrode according to the present invention. The experimentally prepared cell has a JIS LR44 size. The volumes of the amalgamated zinc powders for the negative electrodes were unified so as to be 80 mAh. Table 2 shows variation in total height with respect to discharge duration when the experimentally prepared cells are discharged while setting a final voltage to be 0.9 V at a resistance of 5.1 Ω at 20°C after preservation at 60°C.

Table 2

Amalgamation Rate		1%	3%	5%	7%
	Discharge Duration				
Amalgamated Negative	<u>n=4 (hr)</u>	36	40	42	41

Electrode based on mercury oxide powder	Variation in Total Height of Cell				
	<u>n=50 (μm)</u>	+36	-10	-9	-9
	Discharge Duration				
Amalgamated Negative Electrode based on metallic mercury	<u>n=4 (hr)</u>	18	32	41	40
	Variation in Total Height of Cell				
	<u>n=50 (μm)</u>	+186	+58	-10	-9

As can be seen from Table 2, in the case of the negative electrode prepared by the conventional method, the cell is remarkably expanded particularly at an amalgamation rate of 3 % or less, and the discharge performance thereof deteriorates, whereas in the case of the negative electrode according to the present invention, there are no problems in the expansion and discharge performance of the cell even at an amalgamation rate of 3 %, so that the negative electrode of the present invention can be used for a cell.

[Advantageous Effects of The Invention]

As described above, according to the present invention, a method for uniformly carrying out amalgamation using mercury oxide powder, and a method for carrying out amalgamation in a gelled electrolyte, which is capable of preventing zinc from being physically destroyed during amalgamation, are simultaneously carried out to reduce the amalgamation rate while maintaining corrosion resistance as a gelled zinc negative electrode. Thus, it is possible to achieve a low-pollution alkaline cell without any problems in practical performance. In addition, according to the present invention, the gelled zinc negative electrode obtained by amalgamation can be directly used as a negative electrode for a cell, so that all of equipment, materials and so forth for amalgamation treatment, which are required in the conventional method, are not required. Thus, according to the present invention, there is an advantage in that manufacturing costs of the cell can be reduced.

Furthermore, while the mercury oxide powder and the zinc powder have

had a specific grain size in the preferred embodiment, the mercury oxide powder may have a grain size of about 100 microns, and the zinc powder may have a grain size of 50 to 300 microns, which is usually applied to a cell. If the grain sizes are in this range, the same gel electrode can be prepared by maintaining an appropriate ratio of the zinc powder to the gelled alkaline electrolyte. In addition, while the polyacrylic sodium has been used as an electrolyte gelling agent in the preferred embodiment, any gelling agents capable of gelling an alkaline electrolyte may be used. Moreover, there are slight problems in corrosion resistance, cell performance and so forth when the amalgamation rate is 1 % in the preferred embodiment. However, it was confirmed that it is possible to obtain a corrosion-resistant gel negative electrode if corrosion-resistant zinc alloy, to which e.g., indium or thallium is added, is used even if the amalgamation rate is about 1 %, and there is no problem in cell characteristics. In addition, while the button-type alkaline manganese cell has been described in the preferred embodiment, the present invention may be applied to other zinc alkaline cells, such as silver sulfide cells and mercury cells.

4. Brief Description of The Drawing

Figure is a sectional view of a principal part of a preferred embodiment of a button-type alkaline manganese cell according to the present invention.

4: Positive Electrode

6: Separator

8: Gelled Zinc Negative Electrode



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Specification

1. Title of The Invention

Alkaline Cell

2. Claims

(1) An alkaline cell comprising a positive electrode and a gelled zinc negative electrode, wherein said gelled zinc negative electrode mainly includes a coarse zinc powder having a grain size of 70 to 500 microns, and a 5 to 30 wt% fine zinc powder, which has a grain size of 25 microns or less, with respect to the amount of zinc powder is mixed and dispersed in a gelled electrolyte.

(2) An alkaline cell as set forth in claim 1, wherein said fine zinc powder is mixed in a gelled electrolyte including an amalgamated coarse zinc powder to be stirred to be amalgamated.

3. Detailed Description of The Invention

The present invention relates to the improvement of a gelled zinc negative electrode for an alkaline cell. It is an object of the present invention to use a mixture of a zinc powder having a usual grain size of 70 to 500 microns and a fine zinc powder having a grain size of 25 microns or less to uniformly disperse the zinc powders in a gelled electrolyte to increase the surface area thereof to improve the coefficient of use of the zinc powders and to improve the discharge characteristics of the cell.

Conventionally, in an alkaline cell of this type, the grain size of a zinc negative electrode for use therein is generally in the range of from 70 to 500 microns, and the zinc negative electrode is formed after being amalgamated with 5 to 20 wt% mercury. In addition, carboxymethyl cellulose (CMC) or a polyacrylic sodium is used as a thickener, and an alkaline electrolyte, such as potassium hydroxide or sodium hydroxide, is used to form a gelled zinc negative electrode shown by 1 in FIG. 1. Furthermore, in this figure, reference number 2 denotes a positive electrode mixture mainly including manganese dioxide, to which graphite powder is added as a conductive material, and reference number 3 denotes a positive electrode case of an iron case plated with nickel. Reference number 4 denotes a negative electrode sealing plate of a three-layer clad material wherein copper,

stainless steel and nickel are laminated in that order from the inner surface. The negative electrode sealing plate 4 is insulated from the positive electrode case 3 by means of an insulating sealing packing 5 of nylon, and seals the cell. Reference number 6 denotes a separator layer of cellophane, nylon nonwoven fabric or the like.

In the above described conventional alkaline cell, the uniform dispersion and surface area of zinc particles are very important to improve discharge characteristics.

However, in order to ensure a negative electrode zinc powder having an ordinary grain size of 70 to 500 microns in a uniformly dispersed state in a gelled electrolyte on various temperature conditions for a long time, the material of a thickener to be used and the amount of the thickener to be added must be very carefully selected, and a strong gel must be used.

Therefore, in a cell reaction, an excessive amount of thickener must be added by nature. In addition, if the strong gel is used, the amount of free electrolyte in the negative electrolyte is small, and the gel is not tightly in contact with the impregnant and separator.

For that reason, the discharge characteristic is considerably deteriorated particularly during high discharge.

In addition, an attempt to pulverize the zinc negative electrode has been made to increase the surface area thereof. However, if the whole zinc negative electrode is pulverized, it is secondary granulated in the amalgamating operation, or the charging efficiency is deteriorated, so that it is difficult to put the method to practical use.

It is therefore an object of the present invention to provide an alkaline cell which can eliminate all of the above described problems.

Referring to FIG. 2, a preferred embodiment of a cell according to the present invention will be described below. In this figure, reference number 1 denotes a gelled zinc electrode according to the present invention, which is prepared by adding a 5 to 30 wt% unamalgamated fine zinc powder having a grain size of 25 microns or less with respect to the total amount of zinc powder to an amalgamated coarse zinc powder having a usual grain size of 70 to 500 microns and gelling the mixture using CMC as a thickener and potassium hydroxide as an electrolyte. Reference number 2 is a positive mixture of manganese dioxide and graphite powder, and formed in a positive electrode

case 3 of an iron case plated with nickel. Reference number 4 is a negative sealing plate of a three layer clad material of copper, stainless steel and nickel, and reference number 5 denotes an insulating sealing packing of nylon or the like. Reference number 6 denotes a separator or impregnant layer of cellophane, nylon nonwoven fabric or the like.

In a cell with this construction according to the present invention, when the amount of the fine grain zinc electrode having a grain size of 25 microns or less, which is added to the gelled zinc negative electrode, exceeds 30 wt% with respect to the total amount of zinc powder, the charging efficiency is volumetrically deteriorated, and the transitional diffusion of mercury based on the amalgamated zinc having the usual grain size is insufficient, so that hydrogen gas is generated after forming the cell.

To the contrary, when the amount of the added fine zinc powder is less than 5 wt%, the surface area increasing effect is small, and the amount of the zinc powder having the usual grain size is relatively increased. Therefore, in order to achieve uniform dispersion, the strong gel must be used similar to the conventional method, so that it is not possible to obtain the advantages of the present invention.

In the cell of the present invention formed on the above described conditions, the fine zinc powder is dispersed around and between particles of the zinc powder having the usual grain size. Even if the strength of the gel layer is lowered, the zinc particles are difficult to be biased, so that the amount of the added thickener can be decreased. As a result, the strength of the gel decreases, and the negative electrode gel is easily in contact with the impregnant. In addition, a free electrolyte is produced in the negative electrode gel layer, and the electric conductivity of ions and electrons is good. In particular, there is an advantage during high discharge or during low temperature discharge.

In addition, the addition of the fine zinc powder naturally increase the surface area of zinc, and decreases the current density on the negative electrode, so that the coefficient of use of zinc particles is improved.

With respect to the above described alkaline manganese cell according to the present invention and the conventional cell of the same type, the gelled zinc negative electrodes having the following compositions were formed and combined with positive electrodes mixture mainly including

manganese dioxide to prepare five LR44 type cells, and various characteristics thereof were compared.

Negative Electrode of Cell of The Present Invention

Coarse zinc powder having a grain size of 70 to 200 microns
 (Amalgamation Rate: 13.3 %) 45 parts by weight
 Unamalgamated fine zinc powder having a grain size of 7.1 to 9.0 microns
 15 parts by weight
 CMC serving as a thickener 3 parts by weight
 10 mol aqueous potassium hydroxide solution 37 parts by weight

Negative Electrode of Conventional Cell

Coarse zinc powder having a grain size of 70 to 200 microns
 (Amalgamation Rate: 10 %) 60 parts by weight
 CMC serving as a thickener 3 parts by weight
 10 mol aqueous potassium hydroxide solution 37 parts by weight

<u>Cell</u>	Open-Circuit	Short-Circuit	Discharge	Discharge
	<u>Voltage</u>	<u>Voltage</u>	<u>A</u>	<u>B</u>
Cell of The	1.57 V	1.1A	54 min.	12 min.
<u>Present Invention</u>				
<u>Conventional Cell</u>	1.57 V	0.8 A	10 min.	8 min.

Furthermore, discharge is carried out by a discharge specification for a camera. Discharge A denotes a discharge duration (min.) until the voltage reaches a final voltage of 1.2 V after a constant-current discharge at 20 mA at 20°C, and Discharge B denotes a discharge duration (min.) until the voltage reaches a final voltage of 1.2 V after a constant-current discharge at 20 mA at 0°C.

From this result, the alkaline cell using the gelled zinc negative electrode according to the present invention has excellent characteristics in a high discharge at ordinary temperature as well as at a low temperature.

In addition, according to the present invention, since a small amount of fine zinc powder is added to coarse zinc powder to be uniformly dispersed in a gelled electrolyte, it is possible to decrease the amount of a thickener

to increase the amount of the electrolyte, so that it is possible to obtain a gelled zinc negative electrode which has a low gel viscosity and which can be easily treated. In addition, the unamalgamated fine zinc powder is mixed in a gel electrolyte including amalgamated coarse zinc powder to be stirred to be amalgamated with mercury of the coarse zinc powder.

4. Brief Description of The Drawings

FIG. 1 is a sectional view of a conventional button-type alkaline cell, and FIG. 2 is a sectional view of a preferred embodiment of a button-type alkaline cell according to the present invention.

- 1: Gelled Zinc Negative Electrode
- 2: Positive Electrode Mixture
- 3: Positive Electrode Case
- 4: Negative Electrode Sealing Plate
- 5: Insulating Sealing Packing

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